Chemical weathering and riverine solute fluxes, Dominica, Lesser Antilles

A Senior Thesis

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By

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Approved by

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Introduction

Previous studies on weathering rates of high standing islands (HSIs) have shown some of the highest observed rates of chemical weathering and associated CO2 consumption. Additionally, recent geochemical studies of andesitic-dacitic terrains in New Zealand, Guadeloupe, and Martinique, showed silicate weathering rates and CO2 consumption so high that they fall only in the range previously determined for basaltic terrains, which are the highest known globally (Dessert et al., 2003). While andesitic-dacitic material makes up a significant amount of the terrain for HSIs, there is limited information on the riverine solute fluxes from these sites. In order to determine weathering flux from the island, water samples were collected from streams draining different catchments with different lithologies. Samples were collected during different seasons to encompass the expected range of weathering rates for different climatic conditions. These data, along with stream flows and rainfall data can be used to estimate chemical weathering rates on the island and the extent of CO_2 sequestration from weathering. I hypothesize in that silicate weathering fluxes and associated CO_2 consumption were highest in rivers that flowed through fresh Pleistocene tephra material

Goals

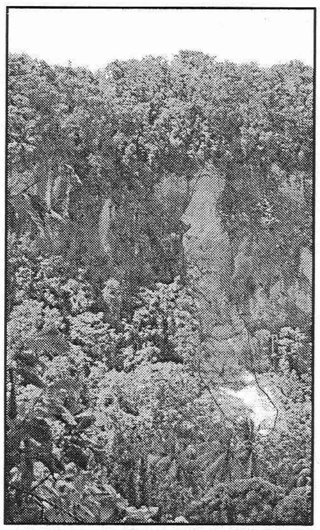
The overall goal of this project is to determine the chemical weathering fluxes in streams whose watersheds are hosted in andesitic-dacitic material on the island of Dominica, Lesser Antilles. The specific objectives of this project are to determine watershed areas of select rivers on Dominica, gauge the selected rivers to determine discharge rate, collect water from the rivers and chemically analyze it for major cation and anions. Data are collected during the wet and dry season to provide an accurate estimate of the annual discharge rates for rivers. The geochemical analysis of the water will be used to calculate the chemical fluxes from individual rivers and overall fluxes for the island. The amount of CO_2 consumed associated with silicate weathering can be determined from the silica flux for a river. Data obtained from each river are then compared to the other rivers on the island that drain areas with different lithologies of different ages. This will determine what role age plays in the ability of the rocks to weather and consume CO_2. The data that are collected can then be compared to similar volcanic terrains from around the world.

Field Area Description

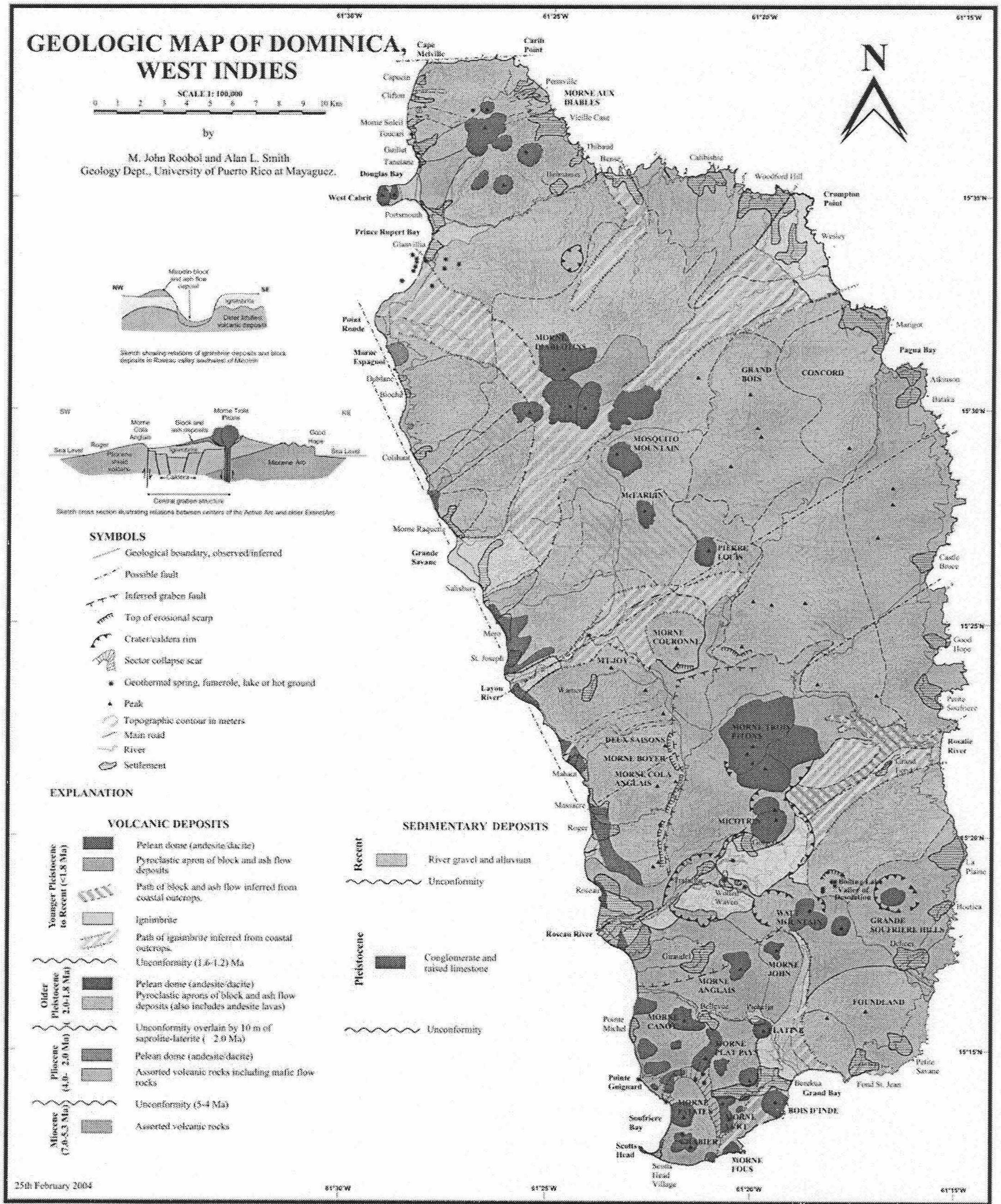
Overview

Dominica is a volcanic arc island in the archipelago that has been created by the subduction of the Atlantic plate beneath the Caribbean plate. The island is located in the Lesser Antilles between the islands of Guadalupe to the north and Martinque, to the south at 15° 25' N, 61°15W (Map 1). Dominica covers 751km^2 of extremely mountainous terrain and has the roughest terrain of any island in the Lesser Antilles, with no contiguous area greater than 1km^2 being flat (Lindsay et al. 2005). The ruggedness is the result of a large number of collapsed volcanic domes. These volcanic domes are expressed as peaks, nine of which are greater than 1000m (Lindsay et al. 2005). These include the second highest peak in the Lesser Antilles and the highest peak in Dominica, Morne Diablotin (1421m) (Sigurdsson and Carey, 1991).

The peaks on Dominica gives rise to one of the highest river densities on the planet. Dominica has streams whose headwaters are above thousands of meters in elevation and thus is considered a high standing island (HSI) by the definition of Milliman and Syvitski (1992). The flanks of some of the volcanoes on the island are extremely steep, particularly in the south where they can be found to be greater than 40° (Reading 1991), resulting in fast flowing streams with extremely steep gradients. The high gradients of these rivers cause incision into the bedrock of many streams. The result of the incision can be seen in picture 1, where the Layou River has incised into its tephra base.



Picture 1: Fresh ignimbrite landslide (red outline) in Layou River valley



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Fieldwork supported by NSF grants EAR 7717064, EAR 9527273, OEDG 01119934 and NASA NCC W-0088.
Note: To print this map at the correct scale of 1:100,000, the 10 kilometer bar scale has to be 10 cm long.

Due its location, prevailing wind conditions, and steep gradients, Dominica receives large amounts of rainfall which results in the incision of many rivers into the bed rock. In the interior rainforest, annual rainfall of up to 10,000 mm has been measured (Reading, 1991) Rainfall has been recorded by NOAA at the Melville Hall Airport on the eastern side of the Dominica (Fig. 1). A 20-year compilation of monthly average rainfall at this site along with temperature, humidity and day length is the only long term assemblage of meteorological data for Dominica.

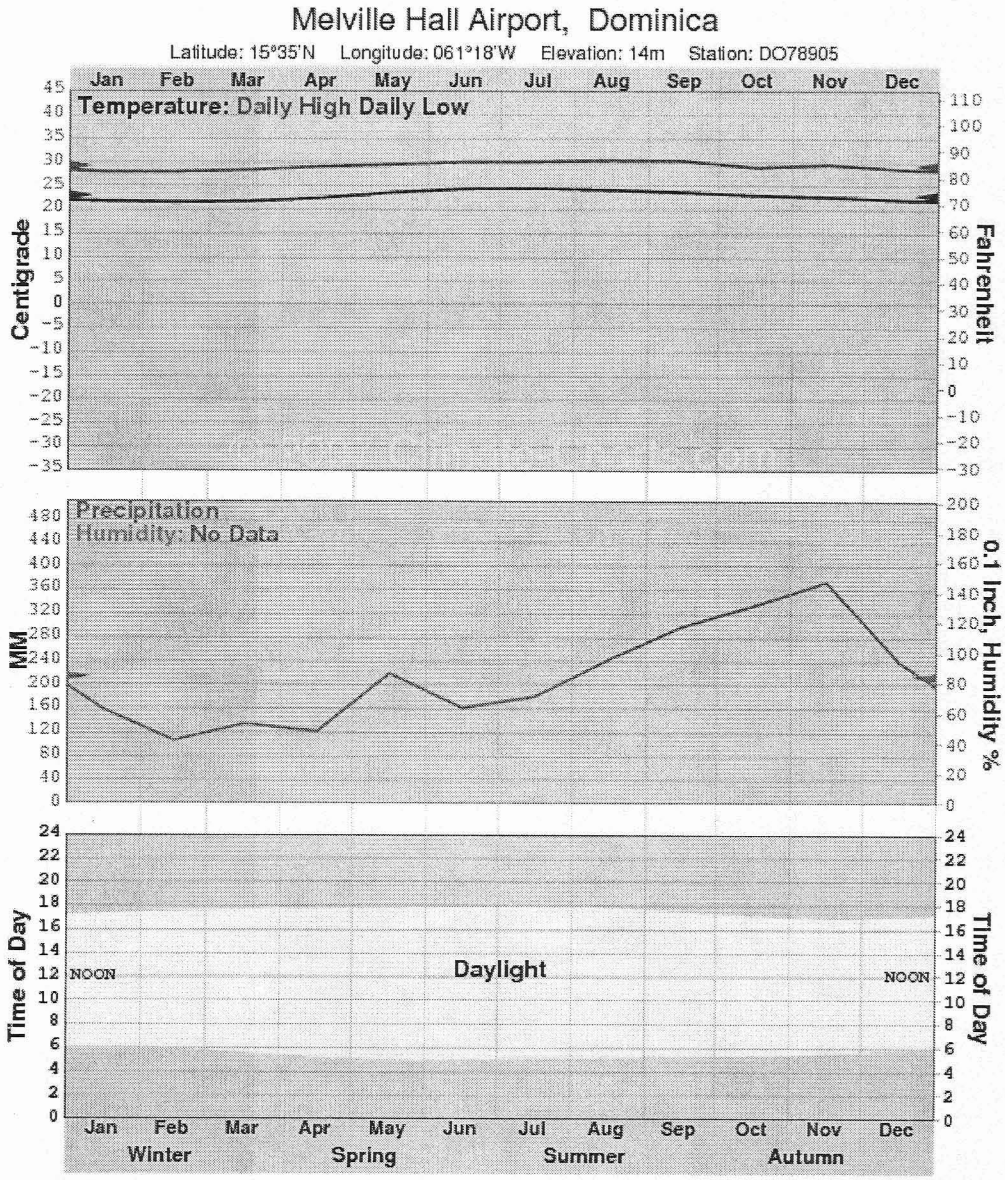


Figure 1. NOAA 20 year compilation of of rainfall, humidity, and daylight for Melville Hall Airport, Dominica, West Indies

(http://www.climatecharts.com/Locations/d/DO78905.php). Average monthly precipitation is 215 mm, but it can vary from a low of ~ 140 mm during the late winter through early spring (Feb, Mar, Apr) increasing throughout the summer to a maximum average of 350 mm in late autumn.

Geology

With the exception of some sedimentary formations along the west coast Dominica's lithology is almost completely composed of Cenozoic volcanics (Gurenko et al. 2005) (Map 1). These sedimentary formations are Pleistocene age conglomerates and limestones found along the west coast of the island. As the island formed coral, coastal conglomerates, and deltaic formations were uplifted and can be found sporadically up to 190m above sea level (Sigurdsson 1972).

Volcanics

Volcanism due to subduction began to create the Lesser Antilles during the Oligocene (Meschede & Frisch 1998). To the north of Dominica two distinct lines of the volcanic arc can be seen. This is the result of a westward shift in the volcanism from 7-20Ma (Smith et al. 1980). Dominica and the islands to its south were created by a combination of these two events. The oldest surfical volcanic rocks on Dominica date to ~7 Ma during the Miocene and are built on the remnants of the Oligocene shield volcano (Lindsay et al. 2005, Meschede & Frisch 1998). These are found along the northeast and east coasts of the island and are basaltic-andesite in composition (Sigurdsson 1972; Lindsay et al. 2005). During the Pliocene the magmas began to evolve, and by ~3.7Ma, large basaltic-andesitic stratovolcanoes dominated the volcanics (Gurenko et al. 2005). These Pliocene volcanoes grew on top of the basaltic-andesite shield volcano created in the Miocene. During this time the volcanism was centered in the northern part of the island. Pliocene eruptions created the base for two of the major peak on the northern half of Dominica, Morne Diablotins and Morne aux Diables (Lindsay et al. 2005). In the last 1Ma the volcanic centers have shifted from the north of the island to the south, but Morne Diablotins and Morne aux Diables volcanic centers are still considered potentially active (Lindsay et al. 2005). There are nine potentially active volcanic centers on Dominica giving it one of the highest densities of volcanic centers in the world (Lindsay et al. 2005).

Pleistocene volcanics

At present, there are seven active centers are located on the southern end of the island, and nearly all of these areas have been active in the last 10Ka (Lindsay et al. 2005).). Although there have been multiple eruptions during the Pleistocene, these volcanic rocks are combined into two lithologic units (Map 1). Of these eruptions there is one that is particularly significant. At 28Ka the Trois Pitons-Microtrin volcanic center erupted and produced ignimbrite and welded tuff (Sigurdsson 1972). Outcrops are exposed in Roseau, Layou, and Rosalie river valleys (Map 1). The base of this eruption is composed mainly of pumice and pillian airfall (Sigurdsson 1991). What makes this event of particular importance is the river valleys the eruption of Trois Pitons-Microtrin filled with material. This eruption supplied two of the largest river on Dominica, the Layou and Rosalie Rivers, with fresh tephra material for weathering.

Recent volcanic activity

On January 4, 1880 a phreatic eruption occurred in the Valley of Desolation. The Valley of Desolation is located in the southeast quarter of the island between Watt Mountain and Grande Soufriere Hills (Map 1) An area of $55km^2$ experienced a measureable level of ashfall with the furthest extent measured as far as 19km away (Lindsay et al. 2005). Near the Valley of Desolation up to 6mm of ash fell while only 6mm fell on Roseau (Lindsay et al. 2005). The most recent volcanic activity occurred on July 8–9 1997. Similar to the 1880 eruption, the 1997 eruption was also phreatic and is thought to have originated from the Valley of Desolation. This eruption was much smaller than the 1880 eruption. These eruptions were not dome-building events and only caused steam and gas escapes. Other than minor ash fall these eruption are not responsible for any large depositional events.

Sampling and Analysis Methodology

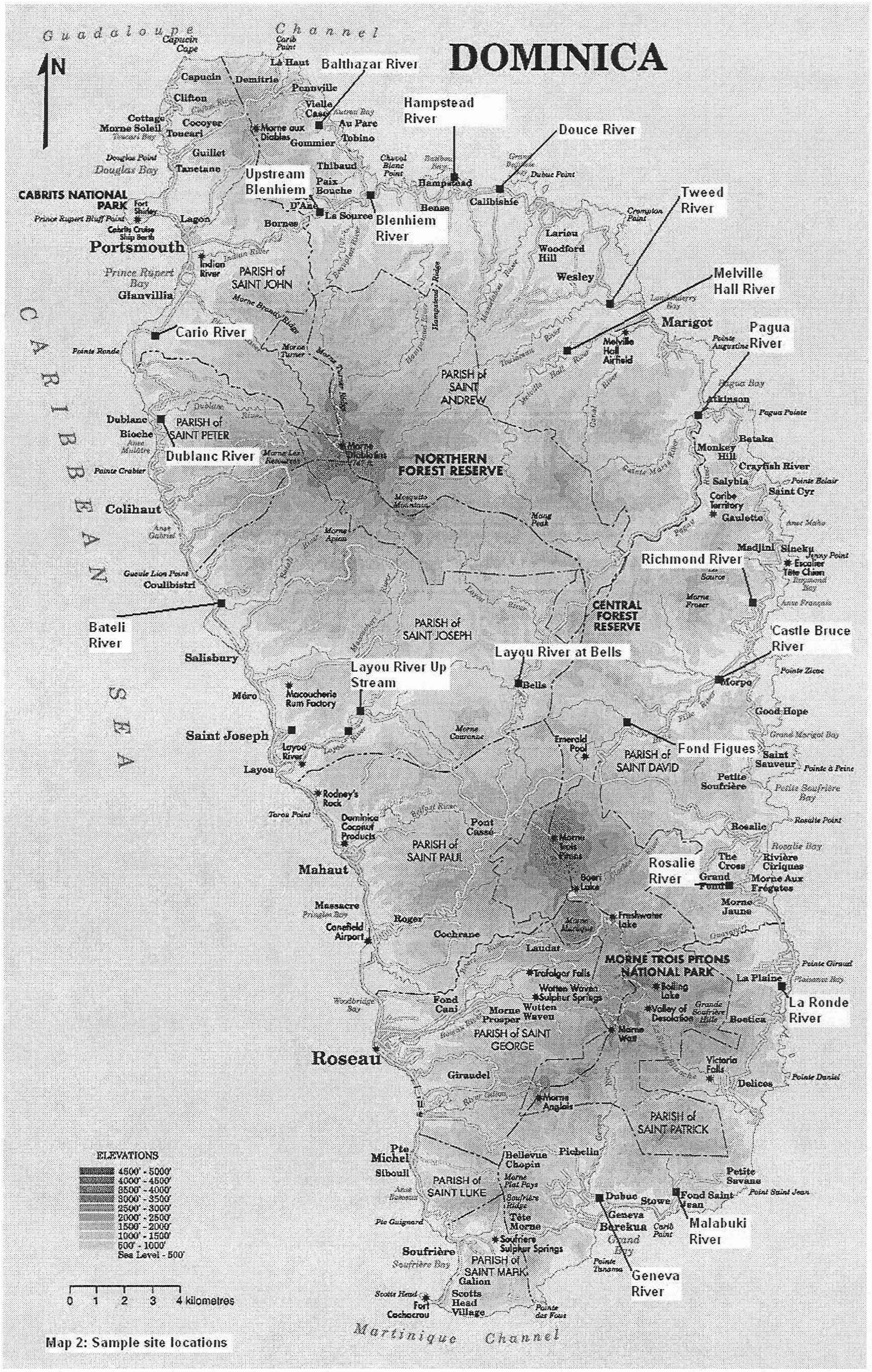
Stream Gauging and Determination of Discharge

Manual gauging of river flow was conducted at 12 rivers during the high-flow season in July, 2006 and at 17 rivers during the low-flow season in March, 2008 (Map 2). Stream gauging and instantaneous stream discharge determination were conducted in accordance with U.S. Geological Survey Method WSP 2175 (Rantz et al., 1992). During the wet season some streams were unsafe to gauge due to high flow, and discharge was not measured. Flow was measured in those streams during the dry season.

A depth profile of the channel was determined at each location prior to using a measuring gauge to obtain flow readings at 20% and 80% above the base of the channel at multiple locations. The product of the distance between two locations in the stream and the depth provided an area to estimate the volumetric discharge. At each location the flow was measured for 30 seconds with a General Oceanic Inc. flow meter. The velocity was calculated from the reading on the flow meter using conversion equations provided by the General Oceanic Inc.

$$v = \frac{n \times 26873}{999999} \qquad \text{(Eq. 1)}$$

Where n is the difference in the start and finishing reading on the flow meter, 26873 is the rotational constant give by General Oceanic Inc. for the specific prop used, and 999999 is a constant used to convert to meters. The distance given in meters is converted to cm and divided by the time to give velocity in cm sec^{-1}. A mean velocity for each



Map 2: Sample site locations are indicated by black squares. (Ottawa-Carleton Geoscience Centre)

location was calculated by averaging the velocity at 20% and 80% above the base of the channel. An estimate of discharge was generated by multiply the average velocity and the depth at the appropriate location and summing this across a stream.

Water Collection and Analysis

Sampling locations were chosen based on the accessibility of the stream. Sites where bridges crossed a stream were choice locations. Stream water samples were collected from 29 locations during the wet season July 2006 and 21 locations during the dry season March 2008 (Map 2). While sampling, if it was raining or began to rain, a second sample was collected on a subsequent day to ensure stream water samples were not diluted by surface runoff. During the dry season some smaller streams were not flowing and water samples could not be collected. At each location, water was collected using a new, 125ml low density polyethylene (LDPE) bottle which had been soaked in 18MΩ deionized water for one week. The bottle was rinsed three times with stream water immediately before sampling. A small aliquot of the sample was then used to measure the pH. The samples were kept in the dark to prevent photosynthesis. Within 12 hours of sampling the bottles were refrigerated until transport back to The Ohio State University. The samples were filtered through Millipore® 0.4μm pore size filters directly into 60ml LDPE bottles. The 60ml LDPE bottle to be used for cation analysis was soaked in HNO_3 for a period of 24 hours and rinsed with deionized water. The 60ml LDPE bottle used for anions was washed with deionized water. Trip blanks were created by filtering deionized water through a 0.4μm pore size filters into new 60ml LDPE bottles. The samples and trip blanks were then shipped to Ohio State and refrigerated at ~4°C.

The cation samples were acidified with concentrated trace-metal grade HNO_3 to a pH of 2–3. Major cation (Li^+, Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) and anion (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, $SO4^{2-}$) concentrations were measure using a Dionex-120® Ion Chromatograph (IC) and the methods of Welch et al. (1996). To determine precision, five replicate check standards were analyzed per run, with relative standard deviations (RSDs) generally more than ±2% but never greater than ±5%. Dissolved Si and Sr^{2+} concentrations were determined using a Perkin-Elmer Sciex® ELAN 6000® inductively coupled optical emission spectrometer (ICP-OES). To compensate for drift in the measurement, external standards were used and check standards were run every 3-4 samples.

Watershed Flux Determination

Watershed areas of sampled streams were determined gravimetrically using 1:25,000 topographic maps because no high resolution digital elevation models exist for Dominica. The watersheds were delineated by tracing them onto tracing paper following the ridgelines that create natural boundaries between the streams. In addition to the watershed, the outline of Dominica was also traced. These outlines were then cut out and weighed. The total surface area of the island is known to be 751km^2. The area of an individual watershed was determined from the mass of the cutout areas normalized to the mass of the cut out area of the island, multiplied to the actual area of the island. Watershed areas are provided in Appendix A. Although the areas of the individual watersheds have not been compiled elsewhere, McDowell et al. (1995) report an area for the watershed draining one of the largest rivers on the island based on U.S Geological

Table 1. Layou Watershed Area Relative Difference

$A_{McDowell}$ =	70.19
$A_{gravimetrically}$ =	76.89
Percent Difference	-9.55

Survey data. They report an area of 70.19 km^2 for the Layou River watershed. This is in good agreement with the area calculated in this study (Table 1)

Results

Stream water samples were collected from 29 locations during the wet season July 2006 (Table 2) and 21 locations during the dry season March 2008 (Table 3). Several of the streams that had been sampled during the wet season in July 2006 were not flowing in March 2008. In addition, the Blenheim and Hampstead Rivers were sampled twice on subsequent days during the wet season to determine the variability in water chemistry over short time scales. A rainstorm on July 13, 2006 caused the stream to be unsafe to gauge, and were gauged on the July 14, 2006. During the wet season some streams were unsafe to gauge by hand and therefore discharge rates were not measured. Those streams that were not gauged in the wet season for safety reason were gauged during the dry season. For most of the larger rivers, discharge rates were roughly two to five fold higher in the wet season than in to the dry season (Table 2 & 3).

Table 2. Dissolved Load of Dominican Rivers, July 2006

River	Sample Number	Sampling Dat	Sample Date Discharge (m^3/s)	pH	TDS mg/kg	Li µmol/kg	Na µmol/kg	NH4 µmol/kg	K µmol/kg	Mg µmol/kg	Ca µmol/kg
Geneva River (DS)	D06-1	11-Jul-06	1.29	7.27	74	0	462	0	44	156	316
Geneva River (US)	D06-3	11-Jul-06	0.02	7.8	77.2	0	819	0	30	147	142
Malabuka	D06-2	11-Jul-06		6.66	83.8	0	546	0	69	130	285
Rosalie River	D06-4	11-Jul-06	3.41	8.03	43.3	0	300	0	30	73	156
La Ronde River	D06-5	11-Jul-06	0.19	7.42	40.5	1	355	0	15	93	153
Mahaut River	D06-6	11-Jul-06	0.02	7.67	44.7	0	371	0	41	88	111
Layou River (DS)	D06-8	12-Jul-06		7.81	46.4	0	375	0	33	94	142
Layou River (US)	D06-23	13-Jul-06		6.73	43.4	0	307	0	30	82	158
Tributary of Layou	D06-7	12-Jul-06	0.17	7.45	65.3	0	638	0	38	137	169
St. Joseph's River	D06-9	12-Jul-06	0.03	7.56	41.3	0	336	0	32	94	142
Bateli River	D06-10	12-Jul-06	0.41	7.72	67.1	0	419	0	36	127	236
Dublanc	D06-11	12-Jul-06	0.42	7.73	104.8	0	993	0	66	291	382
Cairo River	D06-12	12-Jul-06		8	77	0	630	0	52	156	216
Blenheim River	D06-15	13-Jul-06	1.6	7.61	59.4	0	499	0	42	124	194
Blenheim River	D06-27	14-Jul-06		7.29	34.5	0	277	0	25	65	121
Tributary of Blenheim	D06-13	13-Jul-06	0.1	7.46	42.2	0	387	0	57	79	116
Hampstead River	D06-16	13-Jul-06	2.98	7.48	24.7	0	198	0	33	44	64
Hampstead River	D06-28	14-Jul-06		7.45	26.6	0	235	30	68	41	49
Douce River	D06-17	13-Jul-06		6.72	25.9	0	224	0	16	43	94
Tweed River	D06-18	13-Jul-06		6.79	47.3	0	496	0	23	80	167
Melville Hall River	D06-19	13-Jul-06		6.34	22.6	0	159	0	9	36	74
Pagua River (DS)	D06-20	13-Jul-06	1.48	6.91	16.4	0	146	0	12	23	35
Pagua River (DS)	D06-29	14-Jul-06		7.7	23.6	0	185	0	13	40	82
Pagua River (US)	D06-21	13-Jul-06		6.89	31.3	0	242	0	14	59	135
Pagua River (North Fork)	D06-22	13-Jul-06		7.18	46.4	0	472	0	23	94	151
Fond Figues	D06-24	13-Jul-06		7.06	53.7	0	478	0	37	108	165
Castle Bruce River	D06-25	13-Jul-06		7.48	34.9	0	277	0	23	65	121
Richmond River	D06-26	13-Jul-06		7.27	40.5	0	328	0	15	84	194
LODs 1 (umol/kg)						0.14	0.8	24.75	0.01	0.53	1.72
RSDs 1						1.22%	0.51%	1.15%	0.73%	0.52%	1.48%

Sr µmol/kg	Ba µmol/kg	Si µmol/kg	F µmol/kg	Cl µmol/kg	Br µmol/kg	NO3 µmol/kg	PO4 µmol/kg	SO4 µmol/kg	HCO3† µeq/kg
1	0	917	0	232	0	0	0	116	987
1	0	571	0	761	2	1	0	48	567
1	0	1421	4.1	301	0	7	0	29	1075
1	0	602	0	196	0	2	0	33	522
0	0	425	3.7	245	0	1	0	26	562
1	0	579	0	266	0	11	0	17	499
1	0	517	0	315	0	4	0	27	508
1	0	589	0	211	0	0	0	29	549
1	0	575	0	543	1	2	0	35	673
1	0	423	0	246	0	0	3	35	514
1	0	640	2.9	292	0	7	0	152	576
2	0.02	1048	0	637	0	0	0	50	1669
1	0.02	826	0	513	0	1	0	64	783
1	0	620	0	354	0	1	0	56	711
1	0	350	0	211	0	0	0	35	392
1	0.02	338	0	322	0	10	0	31	441
0	0	244	0	174	0	1	0	21	230
0	0	166	0	210	0	3	0	29	244
0	0	233	0	180	0	1	0	23	286
1	0	355	0	374	0	3	0	31	577
0	0	161	4.5	151	0	0	0	50	133
0	0	135	0	146	0	0	0	17	96
0	0	237	0	165	0	0	0	21	235
0	0	319	0	190	0	0	0	27	401
1	0	362	0	375	0	0	0	30	551
1	0	522	0	356	0	1	0	48	608
1	0	362	0	220	0	0	0	33	385
1	0	392	0	248	0	0	0	28	597
0.001	0.002	0.001	2.4	35.1	0.8	0.7	2.8	7.7	
3.60%	7.50%	3.84%	3.71%	0.44%	1.43%	0.43%	3.94%	1.38%	

Table 3. Dissolved Load of Dominican Rivers, July 2008

River	Sample Number	ampling Da	Sample Date Discharge (m^3/s)	pH	TDS mg/kg	Li µmol/kg	Na µmol/kg	NH4 µmol/kg	K µmol/kg	Mg µmol/kg	Ca µmol/kg
Layou Tributary	D08-01	14-Mar-08	0.04	8.02	85.2	2	498	61	435	135	218
Layou River	D08-02	14-Mar-08		8.34	83	2	431	60	377	126	246
St. Joseph River	D08-03	14-Mar-08	0	7.66	103.8	0	686	71	599	170	205
Bateli River	D08-04	14-Mar-08	0.19	7.85	81.8	0	440	53	386	137	207
Dublanc River	D08-05	14-Mar-08	0.25	7.71	102.3	2	465	53	407	141	260
Cairo River	D08-06	14-Mar-08	0.1	7.73	198.5	3	1346	135	1166	511	621
Douce River	D08-07	15-Mar-08		6.63	120	2	796	68	707	186	164
Upstream Geneva	D08-08	15-Mar-08		6.93	128.2	3	596	108	521	150	309
Geneva River	D08-09	15-Mar-08	0.7	8.22	117.4	0	545	77	476	218	405
Malabuka River	D08-10	15-Mar-08		7.26	158.6	0	1056	190	907	438	521
La Ronde River	D08-11	15-Mar-08	0.07	7.53	68	3	414	26	362	127	189
Mahaut River	D08-12	15-Mar-08	0	7.33	78.2	2	456	64	399	126	159
Rosalie River	D08-13	15-Mar-08	1.87	7.73	73	3	367	57	321	101	199
Bleinheim River	D08-14	16-Mar-08	0.43	7.5	111.5	3	659	73	575	193	287
Blenheim Upstream	D08-14A	16-Mar-08	0.04	7.27	140.6	3	806	100	699	249	319
Hampstead River	D08-15	16-Mar-08	1.06	7.71	66.8	2	380	42	333	109	196
Tweed River	D08-16	16-Mar-08	0.01	7.82	64.8	2	386	42	338	115	178
Pagua River	D08-17	16-Mar-08	0.52	8.07	68.2	0	408	24	358	122	282
Pagua North Fork	D08-18	16-Mar-08	0.35	7.81	66.7	2	311	17	273	107	241
Layou River at Belles	D08-19	16-Mar-08	0.37	8.03	63.4	3	332	62	291	84	163
Castle Bruce River	D08-20	16-Mar-08	0.82	8.12	71.5	2	399	30	349	135	296
Richmond River	D08-21	16-Mar-08		5.92	120.4	2	822	31	717	217	331
Limit of Detection						2.4	1.4	0.1	4.4	13.3	22.8
RSDs						4.74%	2.66%	3.03%	2.56%	3.21%	3.17%

Sr µmol/kg	Ba µmol/kg	Si µmol/kg	F µmol/kg	Cl µmol/kg	Br µmol/kg	NO3 µmol/kg	PO4 µmol/kg	SO4 µmol/kg	HCO3† µeq/kg
0	0	887	5	418	0	9	0	33	1204
0	0	1115	0	269	0	2	0	34	1278
0	0	894	3.8	612	3	5	0	36	1410
0	0	1002	0	320	0	1	0	46	1156
0	0	1035	0	344	3	11	0	193	984
1	0	1520	0	907	0	4	0	72	3861
0	0	1178	4.5	641	3	31	0	37	1522
0	0	2110	3.7	353	0	10	2	35	1704
0	0	1340	0	290	3	0	0	157	1734
1	0	821	4.4	897	3	42	0	62	3002
0	0	679	2.7	296	3	2	0	32	1071
0	0	925	4.2	342	0	23	0	20	1082
0	0	987	3.6	234	0	3	0	40	1026
0	0	1076	3.1	512	3	0	2	77	1592
0	0	1524	4.1	664	3	0	0	76	1922
0	0	645	2.5	296	3	0	0	50	964
0	0	628	3.8	305	3	3	0	32	977
0	0	568	3.4	299	0	2	0	35	1223
0	0	365	5.9	254	3	0	0	172	692
0	0	872	3.1	212	3	1	0	24	916
0	0	615	2.6	297	3	1	0	50	1238
0	0	768	2.4	819	3	1	0	35	1773
0.1	0.1	0.7	1.9	43.7	3.4	0.1	1.4	8.8	
14.09%	N/A	3.54%	4.67%	1.59%	1.49%	2.16%	4.58%	2.88%	

Water chemistry

All of the water samples were analyzed for major elements and trace ions. Concentration results and Limits of Detection (LOD) for these analyses are listed in Table 2 and 3

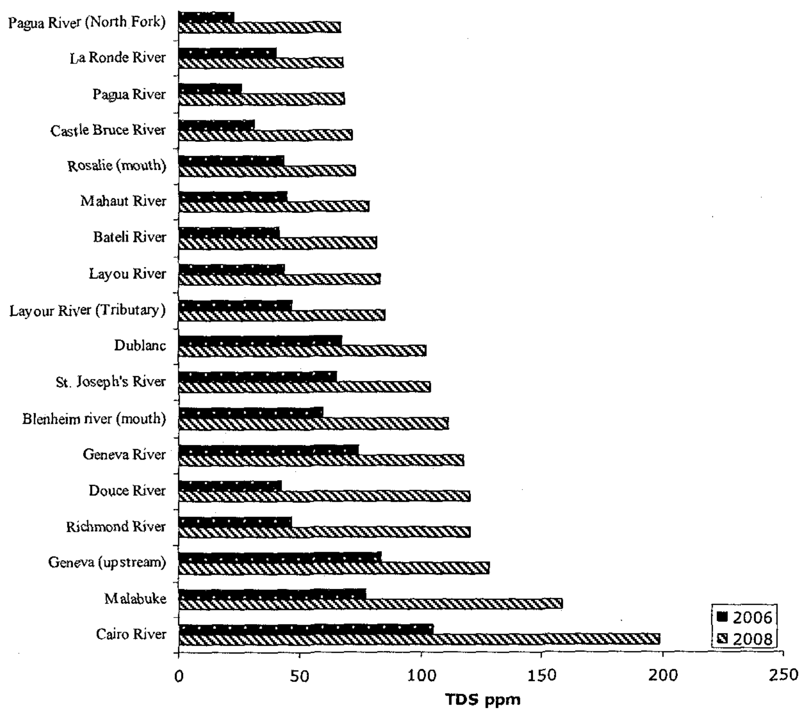


Figure 2. Total dissolved solids determined for rivers of Dominica during the 2006 wet season (black bar with white dot) and 2008 dry season (striped bars).

There was an order of magnitude range in total dissolved solids TDS concentrations in these rivers, from a high of 200 ppm in the Cairo River measured during the dry season, down to only a few 10's ppm for the Pagua River measured during the wet season. (Tables 1 & 2 and Figure 2) Note the solute concentration for the Cairo River exceed those of rivers many times its size. During the July 2006 wet season and March 2008 dry season, the Cairo River (Map 2, Figure 2) has the highest TDS. The Cairo River is a small river which drains younger Pleistocene volcanic material (Map 1). Compare this to the La Ronde and Pagua which drain Miocene and Pliocene volcanics, and have the lowest TDS of the rivers gauged. Solute concentrations in the streams are approximately 1.5 to 3 times greater during the dry season than during the wet season (Figure 2). This reflects in part dilution of weathering products by rainfall and the differences in stream flow; however, the weathering products are different between the wet and dry seasons.

Descriptive statistics were determined for each major ion analyzed to see the range of concentration (Appendix B). A two-tailed Student's t-Test was performed for each ion. The null hypothesis for each test was that the there is no difference between the mean ion concentrations between the wet and dry season ($\alpha = 0.05$). The calculated t values, critical values, and p-values can be found in Appendix B. The null hypothesis of no difference between mean ionic concentrations was rejected for Li, Na, NH_4^+, K, Mg, Ca, Sr, Si, F, Cl, Br and HCO_3^-. The null hypothesis could not be rejected for Ba, NO_3, PO_4 and SO_4.. The results of the statistical analysis show that the major ions concentrations are significantly different between the wet and dry seasons.

Atmospheric input

Three sources of solutes were expected to contribute to the TDS in the streams in Dominica-

- Weathering reactions
- Anthropogenic activity
- Marine aerosols or cyclic salts

Based on previous studies of weathering in volcanic terrains (Dessert et al. 2003, Gaillardet et al. 1999) and weathering of high standing islands, (Lyons et al. 2005 Carey et al. 2006), it was expected that the most significant input of salts to the rivers is from chemical weathering of Dominica's volcanic rocks.. This is important because the weathering of silicates ultimately leads to CO_2 sequestration.

Anthropogenic input of solutes into stream water should be negligible. Dominica was a colony of the British for several hundred years and has the legacy of good infrastructure including water and sewage treatment. The island's population is small and there is little to no industry, so is little input of major ions from industry. A majority of the islands economy is agriculture, particularly cultivation of bananas and other tropical fruits. There is also a large amount of subsistence farming on the interior of the island that uses slash and burn techniques to clear the rain forest. These practices could affect both physical and chemical weathering reactions in the soils. However determination of agriculture's effects on the overall weathering flux from the island is beyond the scope of this study. Input of ions such as NO_3^- and PO_4^{3-} will be due predominately to agriculture, however, these ions contribute little to the TDS measured in the stream water, and do not have a direct impact on silicate weathering reactions.

Solutes from rainfall or from marine aerosols can contribute to the total solutes in rivers on ocean islands. In the Caribbean the prevailing winds blow from the east, bringing storms off the Atlantic Ocean. During the wet season these storms can include hurricanes. Due to Dominica's small size and proximity to the ocean, rainfall or marine aerosols would be important sources of the total salts measured in the streams on this small island in the Caribbean.

Stream water chemistry was corrected for atmosphere input (Tables 5 & 6) using a method modified from Stallard and Edmond (1981). All chloride was assumed to result from sea salt input in precipitation. Contribution of other ions from precipitation was then calculated using rainwater and sea salt ratios of Cl^- to the other major elements (Lindsay et al. 2005). (Table 5 & 6) Dominica is devoid of evaporite deposits and it was assumed that all Cl^- in stream water samples was from precipitation). Rainwater data from El Verde in the Luquillo Experimental Forest, Puerto Rico were used to calculate ratio of Cl^- to Na^+, K^+, Mg^{2+}, Ca^{2+}, and SO_4^{2-} (McDowell et al., 1990) while ratios to Li^+, Sr^{2+}, F^-, and Br^- were determined from sea salt data (Bruland 1983). This is a conservative approach to account for marine input into rainwater, which may result in an underestimation of TDS from chemical weathering. Concentrations of NO_3^-, NH_4^+, and PO_4^{3-} were not corrected because their concentrations in sea water are very low, and it was expected that these had an agricultural source. Silica concentrations were also not corrected because dissolved Si was undetectable in rainwater. The rainfall-corrected solute concentrations were then used to determined the fraction of solutes derived from weathering reactions (Fw). The F_w is calculated using the TDS and TDS_c (Eq.2), where TDS_c is the total dissolved solids due to cyclic salts (Table 4).

Eq. 2 $$F_w = \frac{TDS - TDS_c}{TDS}$$

Table 4. Percentages of Solutes from Weathering and Atmospheric				
Season	TDS mg/kg	TDS (corr) mg/kg	% Cyclic	% Weathering
Wet (July 2006)	1339	815	12	88
Dry(March 2008)	2171	1917	39	61

Because Dominica is a relatively small island of only 751 km^2, it was expected that a significant fraction of solutes in the rivers are derived from either rainfall or marine aerosols. However, when comparing fraction of solutes due to weathering (F_w) vs. TDS (Figure 3) this was not observed.

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Weathering

The composition of the rocks, minerals and soils and the reactivity of these minerals affect the composition of the stream water chemistry. Silicate weathering reactions produce soluble ions and secondary minerals phases. Silicate mineral weathering reactions can be described generally as:

silicate mineral + carbonic acid → soluble cations + HCO_3^- + H_4SiO_4 + Clay minerals

Plagioclase and pyroxene typically dominate the composition of andesitic material. As such, the weathering of these minerals should be reflected in the water chemistry. Weathering reactions for Anorthite(Eq. 3), Albite(Eq.4), and Enstatite(Eq.5) can be described by

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2(OH)_4$$

(Eq.3) Weathering reaction for Anorthite

$$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$$

(Eq.4) Weathering reaction for Albite

$$MgSiO_3 + 2H_2CO_3 + H_2O \rightarrow Mg_2^+ + 2HCO_3^- + H_4SiO_4$$

(Eq.5) Weathering reaction for Enstatite

. It is apparent from the weathering reactions that there are several different soluble species that can be used for estimating weathering flux from stream data. All of these reactions consume acidity and produce base cations and alkalinity, so one method to quantify silicate weathering is to use the Alkalinity (HCO_3^-) (Figure 4) generated as a result of weathering. Alkalinity is calculated by charge balance between cations and anions in solution. A strong positive correlation is observed between alkalinity and the TDS from weathering reactions, indicating that the alkalinity is a robust indicator of weathering (Fig.4) One drawback to using alkalinity is that there maybe input from external sources such as oxidation of organics or the weathering of carbonates.

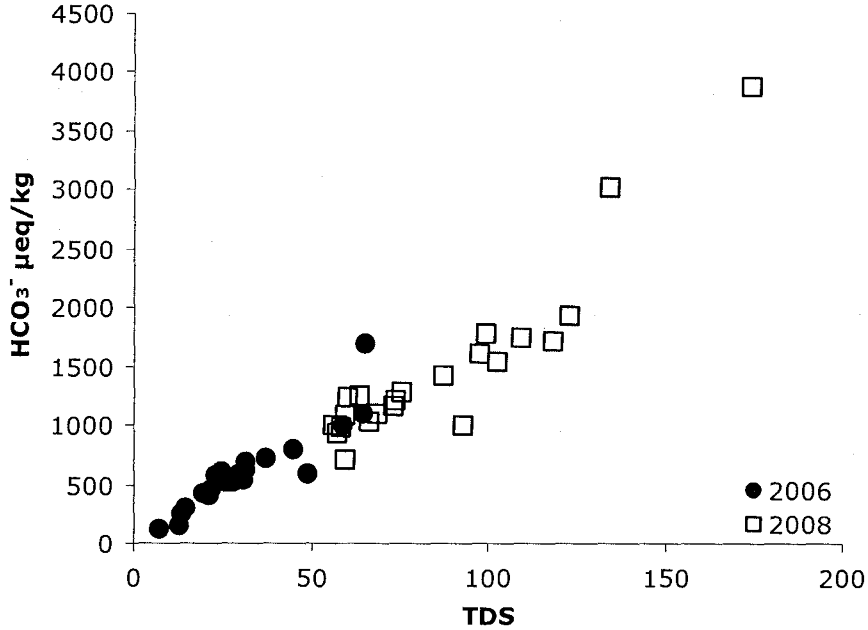


Figure 4. TDS vs Alkalinity. Dry season samples (white squares) have higher concentrations of HCO_3^- than the wet season. This may indicate more weathering in the dry season.

Sum Cations

Another way to calculate chemical weathering is to uses the sum of cations (Ca + Mg + Na + K = TZ^+) (Edmond and Huh, 1997) after correction for atmospheric input. As was observed for alkalinity, there is a strong positive correlation between TZ+ and TDS. The chemical data supports the hypothesis that streams that have the highest concentration of major cations, Ca^{2+}, Mg^{2+}, K^+, Na^+, have watershed that drain fresh tephra material. Again the Cairo River stands out against all others in both the wet and dry seasons as the river with the highest TZ^+. The other two points that over lap with these dry season data are the Upstream Geneva River and Geneva River (mouth) (Figure 4) (Map 1&2). These also flow through Pleistocene volcanic rock

While these wet season data supports the hypothesis that fresh volcanic tephra material may weather more easily, there are results from streams in the dry season that do not. These streams are the Malabuka and Upstream Blenheim Rivers. Both are small watersheds with low flow rates but have extremely high TZ^+ and TDS.

Although there is a good correlation between the TZ+ and TDS, the relative abundances of major ions varies among the streams and over the two different sampling periods. In Fig. 5 the relationship between Si and Na + K/Ca+Mg is characterized.

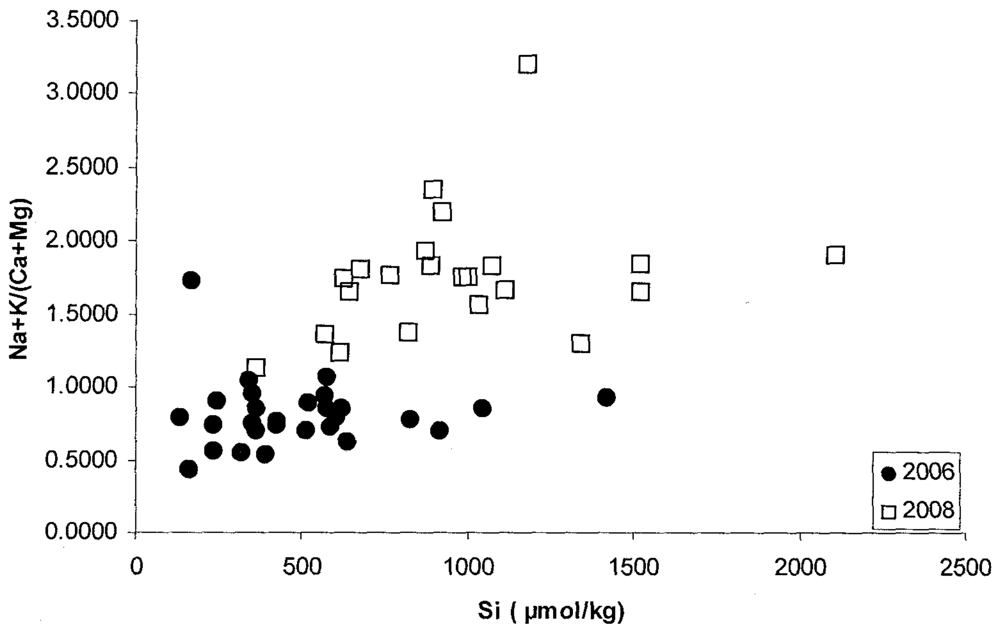


Figure 5. Si vs. Na+K/(Ca+Mg) plot shows enrichment of divalent cations in Dominican rivers during the wet season (solid circles).

This plot shows that during the March 2008 dry season the relative proportions of Na and K are enriched compared to Ca + Mg. In addition, this plot shows that during the wet season there is an enrichment of divalent cations in the streams. It is not clear whether the divalent ions are drawn out during the wet season or if the ions are precipitating in situ during the dry season.

The weathering flux can also be estimate by using the amount of silica in solution. The relationship between Si concentration and TDS show two distinct linear relationships (Fig.6). The wet season samples have lower silica concentrations, most likely due to dilution effects of rainfall. The dry season samples have higher TDS. It was decided to use the Si method to estimate for chemical weathering because there are fewer corrections that need to be performed on the chemical data.

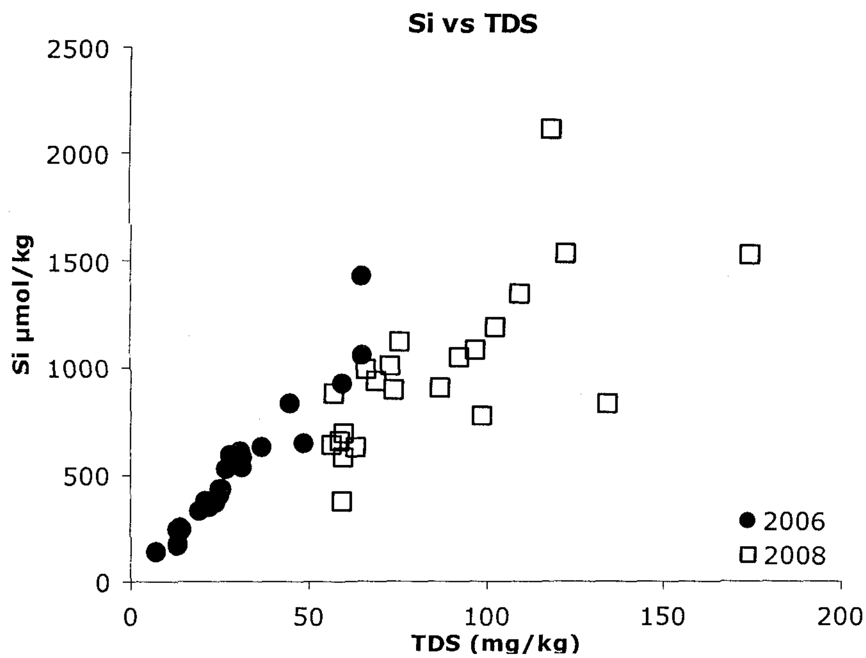


Figure 6. Si vs. TDS. The total concentration of silica increased during the dry season (white square). This indicates a higher degree of chemical weathering

Discussion

Weathering flux

The weathering flux from the island can be determined as the product of stream flow and stream chemistry. The composition and concentrations of major ions due to weathering are different in the different streams depending both on lithological and hydrological variables. By using Si concentration to gauge chemical weathering, the relationship between the weathering flux, catchment size and discharge can be explored (Fig. 7 & 8). There is very small negative (Appendix C) correlation between watershed area and Si concentration (Fig. 7). There are tributaries or upstream locations that were sampled and or gauged for discharge that do not have watershed areas calculated, and are subsequently excluded from this plot. There is a $p \approx 0.80$ for both the wet and dry season that the addition of more data might change these results. Although there is little correlation between watershed area and Si concentration, it should be noted that the largest density of river with Si concentrations greater than 500μmol/L have watershed areas between 1.8 to 10km^2.

Fig. 8 exhibits a negative correlation between stream discharge and Si concentration (Appendix C). It is hard to draw any conclusion from this plot because many streams are excluded due to lack of flow data for either the wet and or dry season for reasons stated previously. In addition there are tributaries or upstream locations that were sampled that do not have watershed areas associated with them. As previously seen (Figure 2) the Cairo River and Malabuka Rivers have some of the the highest TDS in both seasons, but with out flow it could not be plotted. There is a $p = 0.18$ for the wet season and $p = 0.56$ for the dry season, that more data might change the trend of these data. More data would be required to ascertain the true relationship between discharge and Si concentration.

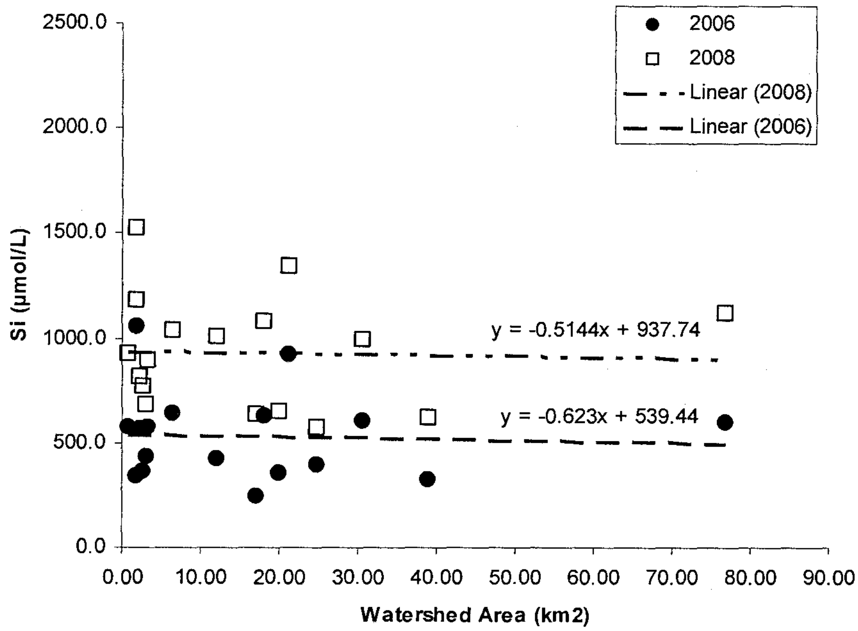


Figure 7. Si concentration. Vs. Watershed Area concentration shows a slight negative trend, but for both wet and dry seasons data there is p-value ≈ 0.80 that more data might change these reulsts.

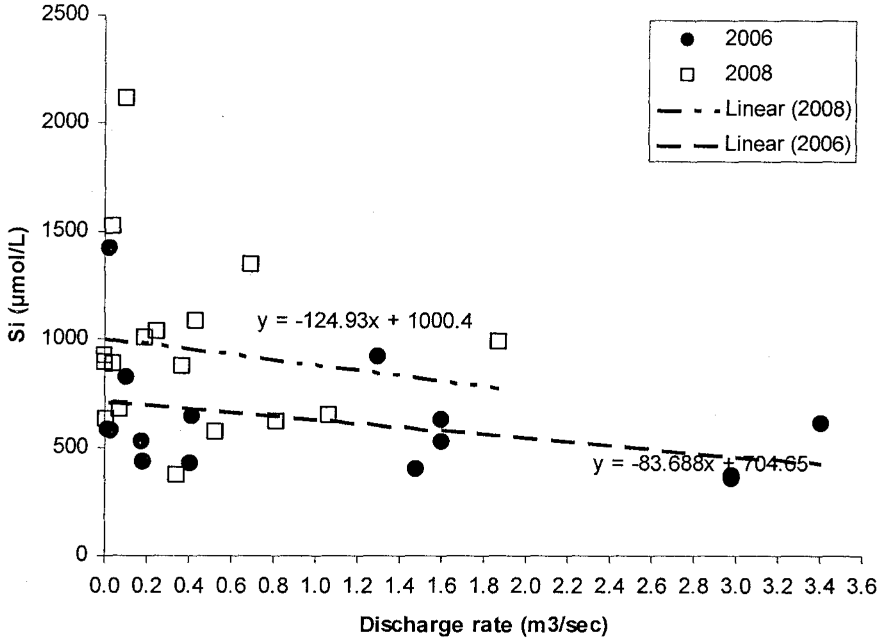
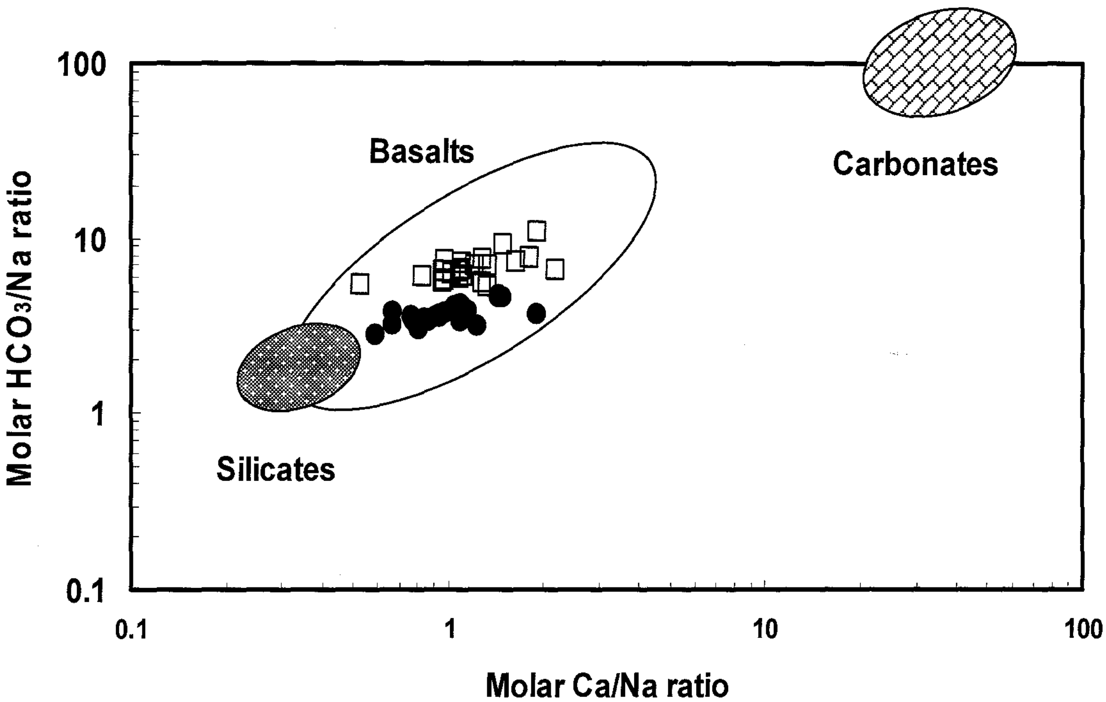


Figure 8. Si concentration vs. Discharge shows a negative relationship, but for both wet and dry seasons data.

After correction of the cation and anion concentrations for rain water, log-log plots of the molar ratios of Mg/Na vs. Ca/Na and HCO_3/Na vs. Ca/Na were created (methods of Gaillardet et al. 1999) (Fig 9 & 10). These elemental ratios were chosen because they exhibited the best correlation of ratios out of Ca/Na, K/Na, Mg/Na, Cl/Na, SO_4/Na, and HCO_3^- (Gaillardet et al. 1999). These plots allow comparison to similar terrains worldwide.

Carbonate weathering is plotted in a region that has a high Ca/Mg molar ratio because there is very limited dolomite deposition occurring at present. The region for silicate is based on average composition of granitic rock. From Dessert et al.'s (2003) basaltic weathering data, an area for average basalt composition was determined. The andesitic-dacitic terrain of Dominica is weathering more like basaltic rock than granitic rock (Figs. 9 & 10). This observation lends support to the hypothesis that the weathering of andesitic rocks is important and should not be combined with bulk silicate weathering in determining global values.



Figures 9 & 10.:
ions normalized to
carbonates, silicate
global averages
Dessert et al. 20
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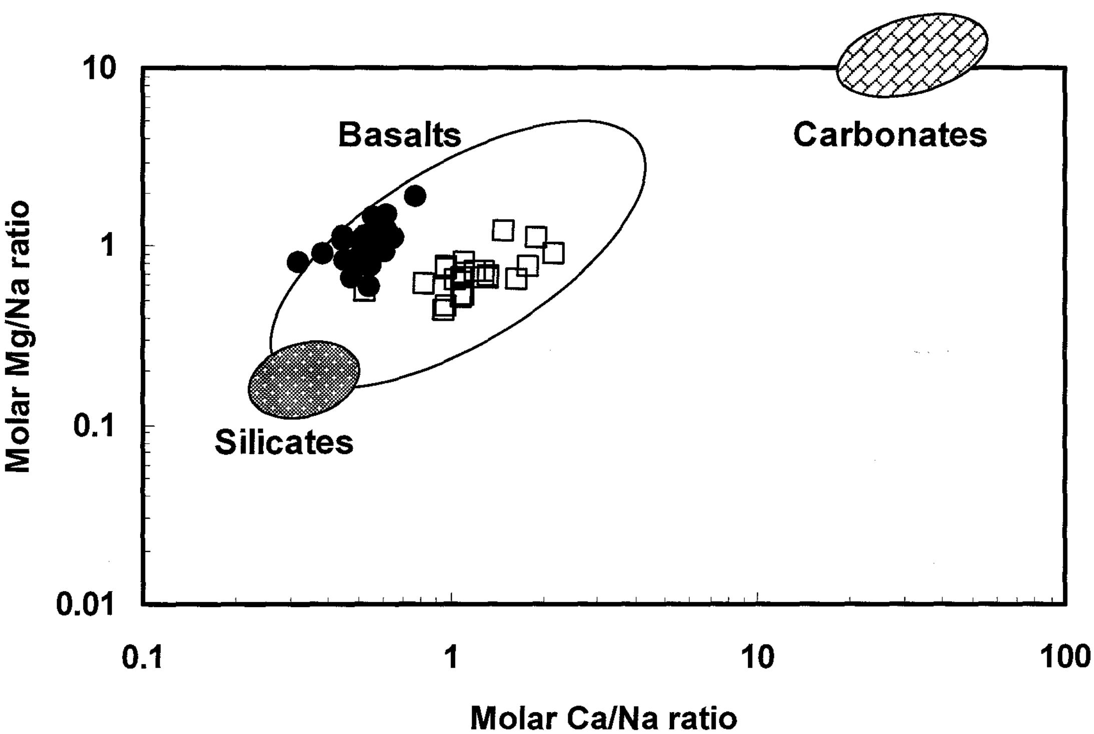

Table 5. Si weathering yield July 2006 & March 2008		
River	July 2006 H_4SiO_4 Yield, t $km^{-2}a^{-1}$	March 2008 H_4SiO_4 Yield, t $km^{-2}a^{-1}$
Geneva River (DS)	35.48	39.19
Rosalie River	39.41	53.46
La Ronde River	16.77	14.33
Mahaut River	6.70	3.17
Layou	51.03	55.44
St. Joseph's River	2.01	0.05
Bateli River	9.21	13.92
Dublanc	24.23	34.67
Blenheim River	32.21	22.87
Hampstead River	33.78	30.39
Pagua River (DS)	9.13	10.69

On geologic time scales the weathering of silicate rocks acts like a global thermostat (Walker et al. 1981). As the calcium bearing silicates react with CO_2 they release their Ca^{2+} into solution and create HCO_3^- and a clay mineral (Eq. 5). The free Ca^{2+} ion reacts with the HCO_3^- to form calcite and water (Eq. 6). Through these reactions CO_2 is drawn out of the atmosphere and sequestered into the oceans, and over a long enough time period this reduction of atmospheric CO_2 can cool the climate.

$$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + 2HCO_3^- + Al_2Si_2(OH)_4 \qquad \text{(Eq.5)}$$

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2 + 2H_2O \qquad \text{(Eq.6).}$$

Silicate weathering yields (ØSi) and associated CO_2 consumption ($ØCO_2$) for each watershed are calculated using the methods of Edmond and Hun 1997. The relationship between the silica flux and CO_2 consumption is estimated to be $ØCO_2 = 2ØSi$ (Edmond and Huh, 1997). This method is more robust that other methods because it requires only a minimal number of corrections in the data. With this method the silica fluxes and annual silica yields and associated CO_2 consumption values were generated. A maximum and minimum for the H_4SiO_4 yield during the two sampling seasons (Table 5) were calculated in tons $km^{-2} a^{-1}$. This calculation is done by multiplying Si concentration in tons by the annual discharge and normalizing it to the watershed area. These estimates are calculated without adjustment for the wet and dry season discharge and solute data. The Si weathering flux for the gauged rivers ranges from 2.01 to 51.03 t $km^{-2}a^{-1}$ in the wet season and from 0.05 to 55.44t $km^{-2}a^{-1}$ in the dry season.

In order to calculate the CO_2 consumption the Si weathering flux must be converted from tons $km^{-2} a^{-1}$ to moles $m^{-3}a^{-1}$. After calculation of the Si flux in mols $m^{-3}a^{-1}$, this value is multiplied by two in accordance with $ØCO_2$ = 2ØSi (Table 6). These calculations do not take seasonal variation into account and only offer a single, instantaneous value for each of the two seasons. The CO_2 consumption values for the wet season range from 143 $x10^3$ to $3634x10^3$ moles $km^{-2}a^{-1}$ in the dry season to $146x10^3$ to $4093x10^3$ moles $km^{-2}a^{-1}$.

Table 6. CO_2 Consumptions July 2006 & March 2008

River	July 2006 CO_2 Flux, x 10^3 moles $km^{-2}a^{-1}$	March 2008 CO_2 Flux, x 10^3 moles $km^{-2}a^{-1}$
	Wet Season	Dry Season
Geneva River (DS)	2526	3287
Rosalie River	2806	4093
La Ronde River	1195	1445
Mahaut River	477	559
Layou	3634	3948
St. Joseph's River	143	146
Bateli River	656	935
Dublanc	1726	2547
Blenheim River	2293	2859
Hampstead River	2405	2922
Pagua River (DS)	650	829

To calculate the annual flux for a watershed, the precipitation needs to be taken into account. Rainfall greater than 180 mm $month^{-1}$ is deemed to be indicative of the wet season (Table 7). Using this I determined that seven months of the year are deemed to be wet season and five months are dry season.

The weighted flux (Table 8) for a stream is calculated by find the flux for seven months of wet season and five months of dry season and summing the two values. Discharge and Si concentration for the corresponding season are used so the annual flux reflects what is happening on the island seasonally.

Table 7. Monthly Precipitation at Melville Hall Airport, Dominica													
Precipitation	**Jan**	**Feb**	**Mar**	**Apr**	**May**	**Jun**	**Jul**	**Aug**	**Sept**	**Oct**	**Nov**	**Dec**	**Average**
Mean Monthly Value (mm)	159	107	135	122	220	162	181	243	298	334	374	240	214.58

Silicate weathering fluxes and associated CO_2 consumption for Dominica exceed all previously established values for andesitic/dacitic terrains (Table 8). Three of Dominica's rivers, the Geneva, Layou and Rosalie, have CO_2 consumption that surpasses the maximum value from Taranaki Region, New Zealand (Goldsmith et al. 2008). Of the nine other river on Dominica that have fluxes determined, all fall with in the range of values for the Taranaki Region. Dominica's lithology of andesite/dacite should weather at an order of magnitude slower than basaltic rocks based on laboratory experiments (Wolff-Boernish et al. 2006). The islands to the north and south of Dominica, Guadelupe and Martinique are predominantly basaltic-andesitic terrains and should be expected to weathering more quickly than Dominica. On Dominica, seven of 11 rivers for which yields can be calculated have silica yields and associated CO_2 consumption greater than those reported for Guadeloupe and Martinique (Dessert et al. 2001).

Table 8. Silicate Weathering Yields and CO_2 Consumption in Dominica weighted for seasonal rainfall			
River	**Area Upstream of Sampling Location (km^2)**	**H_4SiO_4 Yield, $t\ km^{-2}a^{-1}$**	**CO_2 Flux, x 10^3 moles $km^{-2}a^{-1}$**
Geneva River (DS)	21	46.1	3287
Rosalie River	31	57.5	4093
La Ronde River	3.0	20.3	1445
Mahaut River	0.8	7.9	559
Layou	70	55.4	3948
St. Joseph's River	3.4	2.1	146
Bateli River	12	13.1	935
Dublanc	6.5	35.8	2547
Blenheim River	18	40.2	2859
Hampstead River	20	41.0	2922
Pagua River (DS)	25	11.6	829
Other Rivers			
Taranki Region, New Zealand[a]	---	3.1-33.6	217-2926
Martinique and Guadeloupe[b]	---	---	1100-1400
Andes[c]	---	---	220-1000
Himalayas[c]	---	---	100-320
Deccan Traps[d]	---	---	580-2540
Reunion Island[e]	---	---	1300-4400

[a]*Goldsmith et al. [2008],* [b]*Rad et al. [2006],* [c]*Edmond and Huh [1997],* [d]*Galy and France-Lanord [2001],*
[d]*Dessert et al. [2001],* [e]*Louvat and Allegre [1997]*

When the seasonal discharge and Si concentration weighted averages for CO_2 consumption by weathering in Dominica's streams are compared to other regions around the world it is apparent that Dominica is has very high weathering fluxes and CO_2 consumption. Silicate weathering fluxes and associated CO_2 consumption for Dominica exceeds all previously established values for andesitic/dacitic terrains (Table 8). The Rosalie and Layou Rivers surpass the Taranki Region of New Zealand by 1000 moles $km^{-2}a^{-1}$. This is 28% larger than highest know andesite weathering rates. Additionally, Dominica CO_2 consumption rates fall within range of those previously established for basaltic terrains such as the Deccan Trap and Réunion Islands (Galy and France-Lanord 2001, Dessert et al. 2001, Louvat and Allègre 1997).

From the comparison of the data it is clear that Dominica's andesites weather more quickly than basalts. This is largely due to the lack of crystallinity of the tephra on Dominica. The number of Si-O bonds that occur in a silicate and how these bonds are linked together controls the dissolution rates of silicates (Wolf-Boenisch et al. 2006). These data support the hypothesis in that silicate weathering fluxes and associated CO_2 consumption were highest in rivers that flowed through fresh Pleistocene tephra material (Table8, Maps 1 &2).

The tephra makes an excellent weathering substrate especially when it is delivered directly to the rivers. Recent work had tried to link the physical and chemical erosion rates (Carey et al. 2006, Lyons et al. 2005). The high slope gradients on Dominica cause instability resulting in landslides (Reading 1991). The instability is increase with precipitation, with also increases. When a landslide does occur (Picture 1), it generates fresh surface area to weather. This repeatedly happens and leads to the high silicate weathering flux and CO_2 consumption observed for Dominica.

Conclusions

Silicate weathering rates and CO_2 consumption determined for Dominica are among the highest ever determined in the world. Dominica's silicate weathering flux and fall within ranges previously determined only for basalt. Calculated weathering yields demonstrate importance of HSIs, particularly those with volcanic terrains, when considering global CO_2 consumption. The high weathering rates result from a combination of factors. Lack of crystallinity in tephra material linked with the high rainfall rates on the interior of the island provides ideal conditions for chemical weathering (Wolff-Boernisch et al. 2006). High slope gradient and river incision set up excellent conditions for landslides to deliver fresh material to rivers for weathering. The fresh tephra material on Dominica in combination with high annual precipitation, climate and high slope suggest the importance of andesitic terrains of similar characteristic as being very important to include in the annual global carbon flux.

To be certain that the contribution associated with andesite is accurate more terrains need to be studied. Other HSI such as Indonesia, the Philippines and Papua New Guinea are good candidates for research of this nature. As sub-polar regions become more temperate the Aleutian Islands may reveal themselves to be a source of chemical weathering as well as another potential study site.

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Appendix A

Watershed Areas and Seasonal Discharge	
River Name	**Watershed area**
Layou Trib	
Layou River	76.9
St.Joseph	3.4
Bateli River	12.1
Dublanc River	6.5
Cairo River	1.8
Douce River	1.8
Upstream Geneva	
Geneva River	21.2
Malabuke River	2.2
LaRonde River	3.0
Mahaut River	0.8
Rosalie River	30.6
Bleinheim A	18.1
" B	
Blenheim Upstream	
Hampstead A	20.0
" B	
Tweed River	17.1
Pagua River	24.7
Pagua N. Fork	
Layou River at Belles	
Castle Bruce River	39.0
Richmond River	2.7

Appendix B

Discriptive Statistics:Wet Season, July 2006 Water Chemistry

	Li	Na	NH4	K	Mg	Ca	Sr	Ba	Si	F	Cl	Br	NO3	PO4	SO4	~HCO3	TDS
Mean	0.03	398	1.08	33.1	95	156	1.59	0.00	497	0.54	301	0.117	1.951	0.123	41	551	47891
Standard E	0.03	37	1.08	3.3	10	15	0.15	0.00	54	0.26	28	0.083	0.573	0.123	6	60	4040
Median	0.00	363	0.00	31.3	86	146	1.52	0.00	424	0.00	247	0.000	0.888	0.000	31	538	43425
Mode	0.00	#N/A	0.00	#N/A	#N/A	#N/A	#N/A	0.00	#N/A	0.00	#N/A	0.000	0.000	0.000	#N/A	#N/A	#N/A
Standard D	0.14	197	5.74	17.2	54	78	0.79	0.01	287	1.37	150	0.438	3.031	0.653	29	315	21377
Sample Va	0.02	38787	33	297.4	2885	6069	0.63	0.00	82545	1.88	22632	0.192	9.188	0.426	850	99226	4.57E+08
Range	0.73	847	30.37	60.4	268	346	3.81	0.02	1286	4.50	615	1.917	10.844	3.454	135	1578	88589
Minimum	0.00	146	0.00	8.9	23	35	0.39	0.00	135	0.00	146	0.000	0.000	0.000	17	97	16393
Maximum	0.73	993	30.37	69.3	291	382	4.21	0.02	1421	4.50	761	1.917	10.8	3.454	152	1676	104981
Sum	0.73	11153	30.37	927.5	2653	4369	44.54	0.06	13929	15.20	8435	3.289357	54.6	3.454	1142	15441	1340941
Count	28	28	28	28	28	28	28	28	28	28	28	28	28	28	28	28	28

Discriptive Statistics: Dry Season, March 2008 Water Chemistry

	Li	Na	NH4	K	Mg	Ca	Sr	Ba	Si	F	Cl	Br	NO3	PO4	SO4	~HCO3	TDS
Mean	1.9	572.6	65.7	499.8	177.2	272.5	0.4	0.0	980	2.8	435.5	2.2	6.9	0.2	61.4	1469.6	98689.5
Standard	0.2	55.3	8.5	47.7	22.5	24.9	0.0	0.0	83	0.4	47.0	0.4	2.4	0.1	10.4	154.2	7573.9
Median	2.5	460.4	60.9	402.8	135.7	243.5	0.3	0.0	910	3.3	330.7	3.4	2.4	0.0	38.5	1230.4	84069.9
Mode	0.0	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	0.0	#N/A	0.0	#N/A	0.0	0.0	0.0	#N/A	#N/A	#N/A
Standard	1.1	259.3	39.8	223.6	105.6	116.8	0.2	0.0	389	1.8	220.2	1.7	11.1	0.5	48.9	723.1	35524.9
Sample Va	1.2	67247.2	1583.0	50006.2	11142.0	13635.7	0.0	0.0	150969	3.2	48501.3	2.8	123.2	0.3	2389.6	522886.3	1262018719.4
Range	2.8	1035.4	172.8	893.2	426.9	463.0	0.9	0.0	1744	5.9	695.0	3.5	41.9	1.9	173.0	3168.1	135102.8
Minimum	0.0	310.9	17.2	273.0	84.0	158.5	0.2	0.0	365	0.0	211.8	0.0	0.0	0.0	20.3	692.5	63368.6
Maximum	2.8	1346.3	190.1	1166.2	510.9	621.5	1.0	0.0	2110	5.9	906.8	3.5	41.9	1.9	193.3	3860.5	198471.4
Sum	42.8	12596.8	1445.5	10995.4	3898.2	5995.7	8.2	0.0	21555	62.7	9580.7	47.8	152.4	3.6	1349.8	32330.8	2171168.5
Count	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22	22

Water Sample T-Test Value Summary

Species	July 2006 vs. March 2008		
	[Tstat]	Tcritical	P-value
Li+	8.27	2.07	ND
Na+	2.61	2.02	0.01
NH4+	7.56	2.07	ND
K+	9.77	2.08	ND
Mg2+	3.34	2.05	ND
Ca2+	4.03	2.03	ND
Sr2+	7.72	2.04	ND
Ba2+	1.79	2.05	0.08
Si	4.87	2.02	ND
F-	5.01	2.02	ND
Cl-	2.45	2.03	0.02
Br-	5.59	2.07	ND
NO3-	2.04	2.07	0.05
PO43-	0.24	0.24	0.81
SO42-	1.74	2.04	0.09
~HCO3-	5.56	2.05	ND

ND = Not determinable

Appendix C

Regression Statistic Summary

Watershed Area vs. Si **July-06**

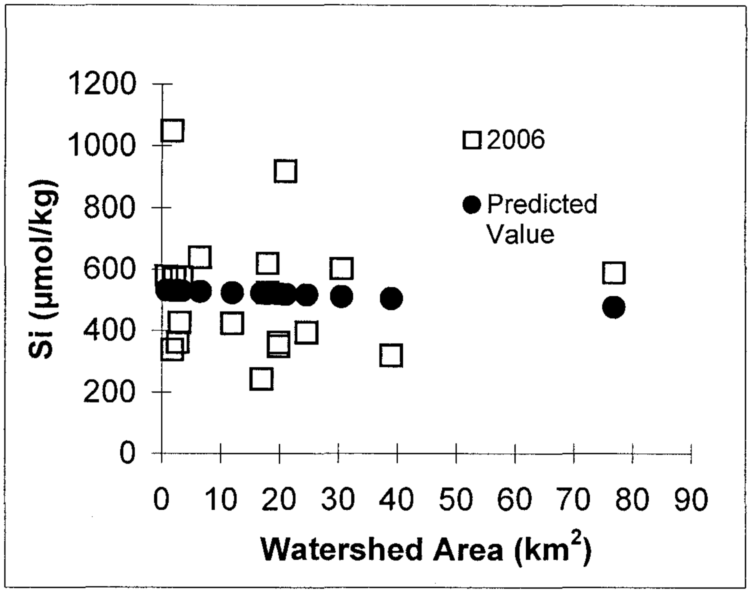
Regression Statistics	
Multiple R	0.06
R Square	0.00
Adjusted R Square	-0.05
Standard Error	208.95
Observations	19.00

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
	1.00	3034.12	3034.12	0.07	0.80
	17.00	742253.55	43661.97		
	18.00	745287.67			

	Coefficients	*tandard Errc*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	531.90	66.01	8.06	0.00	392.63	671.16
X Variable 1	-0.71	2.69	-0.26	0.80	-6.39	4.97

ESIDUAL OUTPUT

Observation	*Predicted Y*	*Residuals*
1	477.29	112.16
2	529.51	45.35
3	523.32	-100.23
4	527.25	112.40
5	530.60	517.63
6	530.62	-192.21
7	516.85	400.39
8	530.34	40.69
9	529.74	-104.25
10	531.31	47.27
11	510.15	92.33
12	519.05	100.87
13	519.05	2.99
14	517.71	-168.07
15	517.71	-155.87
16	519.75	-276.25
17	514.35	-121.91
18	504.16	-185.24
19	529.95	-168.06



Regression Statistic Summary

Stream Discharge vs. Si **July-06**

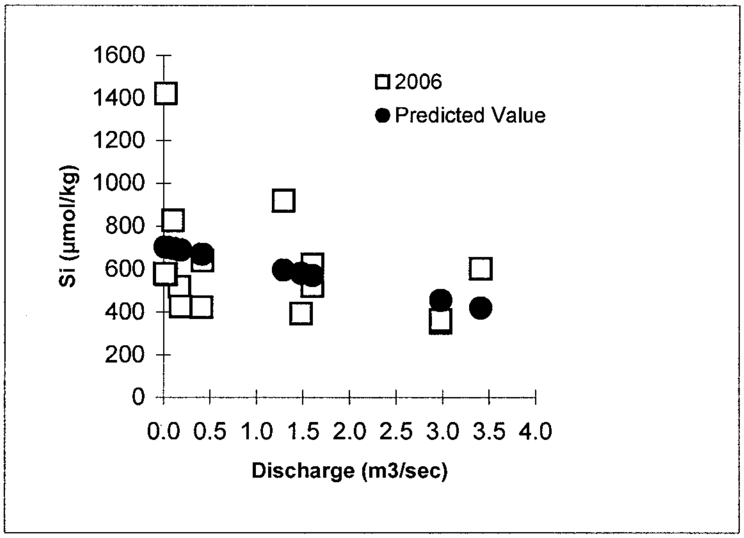
Regression Statistics	
Multiple R	0.36
R Square	0.13
Adjusted R Square	0.07
Standard Error	266.32
Observations	15.00

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1.00	141482.34	141482.3	1.99	0.18
Residual	13.00	922072.11	70928.62		
Total	14.00	1063554.44			

	Coefficients	*tandard Errc*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	704.65	95.32	7.39	0.00	498.72	910.59
X Variable 1	-83.69	59.25	-1.41	0.18	-211.70	44.32

RESIDUAL OUTPUT

Observation	*Predicted Y*	*Residuals*
1	690.18	-172.88
2	702.15	-127.29
3	670.29	-247.19
4	669.59	-29.94
5	702.75	717.99
6	596.45	320.79
7	688.98	-263.50
8	703.28	-124.70
9	419.23	183.25
10	570.67	49.25
11	570.67	-48.63
12	695.92	130.01
13	455.14	-105.50
14	455.14	-93.30
15	580.80	-188.36



Regression Statistic Summary

Watershed Area vs. Si **March-08**

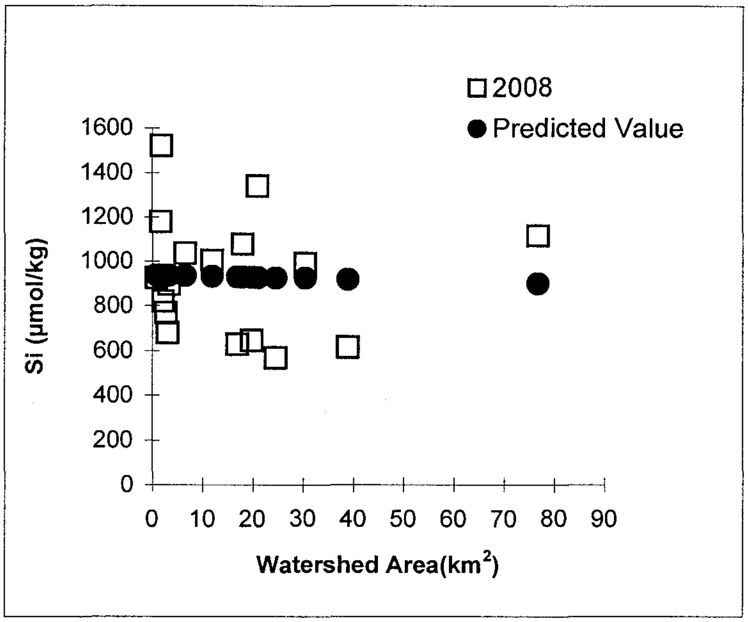
Regression Statistics	
Multiple R	0.04
R Square	0.00
Adjusted R Square	-0.07
Standard Error	277.54
Observations	17.00

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1.00	1588.57	1588.57	0.02	0.89
Residual	15.00	1155417.24	77027.82		
Total	16.00	1157005.80			

	Coefficients	*tandard Erro*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	937.74	89.78	10.44	0.00	746.37	1129.12
X Variable 1	-0.51	3.58	-0.14	0.89	-8.15	7.12

RESIDUAL OUTPUT

Observation	*Predicted Y*	*Residuals*
1	898.19	216.44
2	936.02	-41.77
3	931.54	70.82
4	934.38	101.12
5	936.81	582.84
6	936.82	241.42
7	926.84	412.77
8	936.62	-116.03
9	936.18	-257.18
10	937.32	-12.24
11	922.00	64.76
12	928.44	147.94
13	927.47	-282.83
14	928.95	-300.88
15	925.03	-356.66
16	917.66	-302.24
17	936.33	-168.28



Regression Statistic Summary

Stream Discharge vs. Si **March-08**

Regression Statistics	
Multiple R	0.15
R Square	0.02
Adjusted R Square	-0.04
Standard Error	422.34
Observations	17.00

ANOVA					
	df	*SS*	*MS*	*F*	*Significance F*
Regression	1.00	60748.11	60748.11	0.34	0.57
Residual	15.00	2675569.50	178371.3		
Total	16.00	2736317.61			

	Coefficients	*tandard Erro*	*t Stat*	*P-value*	*Lower 95%*	*Upper 95%*
Intercept	1000.41	133.73	7.48	0.00	715.38	1285.45
X Variable 1	-124.93	214.07	-0.58	0.57	-581.22	331.36

RESIDUAL OUTPUT

Observation	Predicted Y	Residuals
1	995.78	-108.39
2	1000.38	-106.14
3	976.77	25.59
4	969.53	65.97
5	987.37	1122.15
6	912.97	426.65
7	991.36	-312.36
8	1000.01	-74.93
9	766.45	220.31
10	946.21	130.17
11	995.79	528.13
12	867.62	-222.98
13	934.85	-366.48
14	956.94	-591.52
15	954.10	-81.65
16	898.25	-282.83
17	999.75	-371.68